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# PHOTOGRAPHIC REVERSAL BY DESENSITIZING DYES

By Burt H. Carroll and C. M. Kretchman

## ABSTRACT

Latent image on a photographic plate which has been exposed, then bathed in a solution of a desensitizing dye, may be destroyed by a second exposure to light of the proper wave length. Quantitative measurements of the variation of density with wave length were made on plates treated with five desensitizing dyes. In three cases it was also possible to make indirect determinations of the spectral distribution of energy absorbed by the dyed silver bromide; less complete data are available for the other two. There is good correlation between reversal and energy absorption. Where the absorption by silver bromide and by the dye are sufficiently separated in wave length, there are maxima corresponding to each. The Herschel effect in the absence of dyes was negligible, and there is no evidence that it is increased by the dyes. It was demonstrated that safranin may produce either reversal or normal sensitization depending only on the bromide ion concentration. Characteristic curves of the process were made by time scale exposures. The evidence supports the hypothesis that the process is an oxidation, and is the reverse of ordinary sensitization chemically as well as photographically.

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## I. SPECTRAL SENSITIVITY OF THE REVERSAL PROCESS

Positive images of passable gradation may be produced by the following process, the sensitivity being about one-tenth that of a lantern-slide plate so that camera exposures are possible. The plate or film is given a moderate uniform exposure; then bathed in a solution of any one of many desensitizing dyes, preferably with the addition of soluble bromide, dried, and again exposed. The latent image formed by the first exposure is destroyed by the second, and a positive image is formed on normal development. The process is characterized by sensitivity to a wide range of wave lengths, and in many cases the relative sensitivity to the longer wave lengths may be greater than in a good panchromatic emulsion, although the absolute value is much less.

This phenomenon was first observed by Waterhouse,<sup>1</sup> but our knowledge<sup>2</sup> of it is very largely due to the extensive experiments of Lüppo-Cramer, which are now summarized in the latest edition of Eder's *Handbuch der Photographie*.<sup>3</sup> While as a pictorial process it is of very little value, its mechanism is of considerable interest because of its possible bearing on the mechanisms of sensitization and desensitization, and of other reversal phenomena.

The primary object of the experiments to be described in this communication was to determine the relation of the spectral sensitivity of the process to the spectral absorption of the dye which is used. As

<sup>1</sup> Waterhouse, *Proc. Roy. Soc. London*, vol. 29, p. 186, 1875.

<sup>2</sup> No attempt will be made in this paper to give complete references to the extensive literature of dye reversal and the Herschel effect.

<sup>3</sup> Vol. 2, pt. 1, *Grundlagen der photographische Negativverfahren*; vol. 3, pt. 3, *Sensibilisierung und Desensibilisierung*.



already mentioned, the longer wave lengths are usually effective. Lüppo-Cramer has come to the conclusion that the process is essentially the same as the Herschel effect (reversal by red and infra-red radiation on preexposed plates, in the absence of dyes) and that the spectral absorption of the dye "plays only a secondary rôle if at all." Experiments by Mauz,<sup>4</sup> which were made at Lüppo-Cramer's suggestion, were considered as confirming this conclusion. On the other hand, in earlier experiments by one of the writers<sup>5</sup> the maximum reversal corresponded to the maximum absorption by the dye with considerable regularity after allowing for a displacement to the red of about 50 m $\mu$ , like that found in ordinary sensitization.

In this process, results depend on the experimental conditions even more than in normal photography. As it was desired to find the region or regions of maximum sensitivity, the diffraction spectrum was used for exposure because the change of energy with wave length is much less than in a prism instrument. It was essential to avoid overexposure. It is well known that by sufficient exposure it is possible to record a continuous spectrum on an unsensitized emulsion as far as 0.6 to 0.7  $\mu$ , even though the sensitivity in this region is negligible for practical purposes. Stray light in even the best instruments may also give the appearance of continuous sensitivity if the exposure is excessive.

The best apparatus available was a small spectrograph having a concave reflection grating mounted in parallel light, giving a dispersion of 5 m $\mu$ /mm. A Tungsarc lamp was used as the light source. The intensity is quite high, test exposures on fast panchromatic emulsions being made at one twenty-fifth to one-half second, and the stray light is much less than with a transmission grating. This apparatus has been previously used for experiments with methods of spectral sensitization.<sup>6</sup> While the use of the grating spectrograph avoids the great concentration of energy in the longer wave lengths produced by a prism instrument with an incandescent source, the energy from the Tungsarc lamp (color temperature about 3,000° K.) increases so rapidly with wave length that the exposure of the plates to the red end of the spectrum was several times as great as to the blue end.

The test plates were given the white light exposure in a special exposure box, which had been tested photographically for uniformity of illumination. They were then bathed with the mixed solution of desensitizing dye and soluble bromide, swabbed with moist cotton to remove the surplus solution, and dried in a rack designed so that there was unobstructed flow of air over the entire surface of the plate. There are liable to be local irregularities in these plates under the best conditions, and unless the drying is quite uniform, quantitative work is likely to become impossible. The spectrograph exposures were made directly after drying. After the second exposure they were brush developed for four minutes at 20° C. in metolhydroquinone, using the Eastman D-11 formula.

Most of the experiments were done with an experimental pure bromide emulsion. (No. 4-97-2), having a Bureau of Standards speed of 25 and a  $\gamma$  of 0.8 for the above development. This emulsion was used because it was possible to observe the Herschel effect on it under the

<sup>4</sup> E. Mauz, *Zeit. f. wiss. Phot.*, vol. 27, p. 49, 1929.

<sup>5</sup> B. H. Carroll, *J. Phys. Chem.*, vol. 29, p. 693, 1925.

<sup>6</sup> Carroll and Hubbard, *B. S. Jour. Research*, vol. 4 (RP173), p. 693, 1930.

same conditions as the dye reversal; pure bromide emulsions are generally best for this purpose, as they have a minimum of normal sensitivity to the red.

Densities were measured by a physical photometer improvised from a Fabry-Buisson microphotometer. The illuminating system was used to focus a narrow line of light on the plate, and the transmission measured from the deflection of a galvanometer connected directly to a caesium photoelectric cell receiving only radiation transmitted by the plate. Within the range used, the accuracy of the assumption that the deflection was proportional to transmission was of the order of 5 per cent. The photometer obviously is accurate only for low densities, but these were the most important in the reversal work. Densities measured in this way are higher than those determined under diffuse illumination. The wave-length scale was supplied by exposures of the helium spectrum; these could not be superposed on all the reversal plates because the sensitivity was too low, but the scale could be reproduced to 0.2 mm on the plate which is quite sufficient.

The dyes used were as nearly as practicable the same as those used by Mauz.<sup>7</sup> Pinakryptol green and yellow were obtained from the I. G. Farbenindustrie. Fuchsin (pararosaniline) and safranin were Kahlbaum products, believed to be Nos. 646 and 841, respectively, in the Colour Index; phenosafranin was not available, but the toluosafranin is so closely related that no important difference is to be anticipated. Some experiments were also made with the parent dye of the pinakryptol series, 2-*m*-nitrostyrylquinoline dimethyl sulphate, for comparison with those described by Lüppo-Cramer on pages 284-285 of Eder's *Handbuch*, vol. 3, p. 3. This material was synthesized by the research laboratory of the Eastman Kodak Co., from *m*-nitrobenzaldehyde and quinaldine dimethylsulphate at our request; we wish here to acknowledge their generous assistance.

In the previous experiments by Carroll,<sup>8</sup> and by Mauz,<sup>9</sup> the spectral sensitivities of the plates were compared simply with the absorptions of aqueous solutions of the dyes; data for the latter were obtained either from the literature or by relatively crude measurements. We are indebted to Dr. K. S. Gibson and Miss Mabel E. Brown, of the colorimetry section of this bureau, for quantitative data on the spectral absorptions of the dye solutions used in these experiments. It is more satisfactory, however, to know the absorption of the dyed silver bromide, which is the actual absorbing system in the plates. Eder<sup>10</sup> has proved in this way that the maxima of absorption and sensitization actually correspond for some of the sensitizing dyes. Apparatus for transmission measurements on highly diffusing materials like photographic plates was not available, but the absorption maxima were located by measuring the spectral reflection. Silver bromide was prepared by precipitation from equivalent solutions of silver nitrate and potassium bromide, washed five times by decantation, then agitated with approximately 1:5,000 solutions of each of the four dyes, plus a trace of potassium bromide. The silver bromide was considerably peptized by the dyes. The mixture was allowed to stand overnight, and the supernatant solution carefully decanted

<sup>7</sup> See footnote 4, p. 450.

<sup>8</sup> See footnote 5, p. 450.

<sup>9</sup> See footnote 4, p. 450.

<sup>10</sup> Eder, *Photographie mit Bromsilber-Gelatine* (1903 edition), p. 151.



from the silver bromide, which was then suspended in distilled water. This process was repeated twice to eliminate dye not adsorbed to the silver bromide. The final suspension was coated on small pieces of glass, previously coated with a thin gelatin substratum, and dried. The reflection of these samples was measured in diffuse illumination by the colorimetry section. The blackening of the silver bromide under the intense illumination in the spectrophotometer gave considerable difficulty, but error from this source was very largely reduced by rapid readings on a number of samples, measurements being made both on increasing and decreasing wave length. It was, however, impossible to make satisfactory measurements on the sample dyed with pinakryptol green, with its relatively broad and flat absorption bands. All values are relative to the reflectance of a diffusing surface of magnesium oxide, used as a nonselective standard.

Comparison of spectral absorption and spectral sensitivity for each of the dyes may be made from the data presented in Figures 1 to 4. In each of these figures the densities of plates after spectrograph exposures are plotted (in solid lines) as ordinates, against wave lengths as abscissæ. A minimum of density obviously corresponds to a maximum of reversal, and vice versa. The data for spectral absorption are given by the broken lines. Curve 1 in each figure represents the absorbancy (minus log transmittancy) for an aqueous solution of the corresponding dye, at a concentration chosen so as to give a range of logarithms comparable to the other curves. In each case there is a maximum of reversal corresponding to the maximum of absorption by the dye, but displaced by 40 to 60  $m\mu$  toward the longer wave lengths. In Figure 2 the maximum reversal at 465  $m\mu$  obviously corresponds to the principal absorption band of the dye at 430  $m\mu$ ; the change of slope from 590 to 650  $m\mu$  indicates that a faint secondary maximum corresponding to the absorption band at 580  $m\mu$  is superposed on the main curve. The reversal curve for plates bathed with fuchsin (fig. 3) and safranine (fig. 4) have minimum densities at about 420  $m\mu$  in addition to those at 610 and 580  $m\mu$ , respectively, which may be attributed to the dyes. There is no absorption by fuchsin or safranine in the region of 360 to 380  $m\mu$  to account for these minima at 420 to 430  $m\mu$ . The quantitative measurements of spectral absorption by these solutions were carried to 390  $m\mu$  without any indication of a second maximum at shorter wave lengths, and approximate photographic tests failed to show any significant absorption between 400 and 310  $m\mu$ . We are therefore forced to the conclusion that the minima around 420  $m\mu$  correspond to absorption by the silver bromide itself; this conclusion will be discussed more fully later in the paper.

Curve 2 in Figures 1, 3, and 4 represents the spectral reflection of silver bromide dyed with the corresponding dyes; the data are plotted as minus log reflectance, so that a maximum in the curve corresponds to minimum reflectance and maximum absorption. It will be noted that the maxima of these curves are displaced approximately 20  $m\mu$  toward the longer wave lengths from the maxima of absorption in solution. In the case of silver bromide dyed with pinakryptol yellow, the dye and the silver bromide absorb in the same spectral region, so that the two components of reflection can not be distinguished.

Curve 3 in Figures 1, 3, and 4 represents on a logarithmic scale the variation with wave length in the energy radiated by a black body at

3,000° K. The curves in the three figures are displaced vertically by varying amounts to fit the scales of the figures. The color temperature of a Tungsarc lamp is not over 3,000°, and possibly nearer 2,900°. The relative energy incident on the plates may, as a first approximation, be taken as equal to this, since nothing in the spectrograph or illuminating system introduces appreciable selective absorption or reflection in the visible region.

Curve 4 approximates the relative energy absorbed at each wave length from a source of 3,000° color temperature by a material of the reflectance represented by curve 2. In making this calculation, the transmission by the dyed silver bromide was taken as negligible

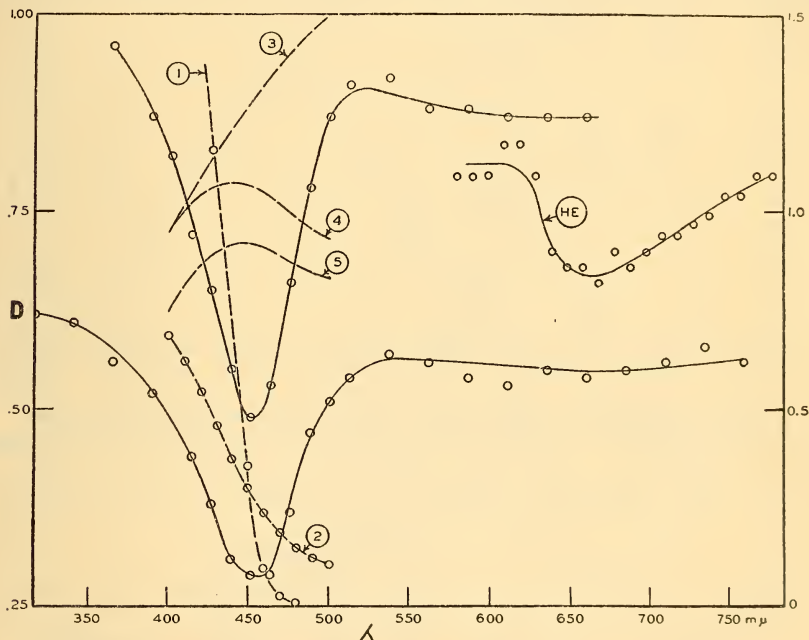


FIGURE 1.—Reversal on plates bathed with pinakryptol yellow and bromide

Solid lines represent densities of plates, on left-hand ordinate scale. The curve marked *HE* is for the Herschel effect on a pure bromide emulsion without dye; 1.5 has been subtracted from all densities to bring the curve on the same plot with the others. Dashed curves (right-hand ordinate scale) are: (1) Absorbancy (minus log transmittancy) of pinakryptol yellow solution, 1.0 g per liter, in 1 cm thickness; (2) minus log reflectance of silver bromide dyed with pinakryptol yellow; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution of energy absorbed from a source such as (3) by silver bromide dyed with pinakryptol yellow; and (5) log quanta absorbed under these conditions

and the absorption as  $(1 - \text{reflectance})$ ; the absorption was multiplied by the relative energy for this wave length, and the logarithm of this quantity plotted. The transmission was not measureable with the available apparatus, but appeared to be not over 10 per cent for the samples actually used for measurement of reflectance. Curve 5 in each of the figures was obtained by dividing the energy absorbed at each wave length by the frequency of the radiation (the inverse of the wave length). This procedure gives the relative number of quanta of energy absorbed. The logarithm of the number was plotted. As curves 3, 4, and 5 all express only relative values, plotted on a logarithmic scale, they have been shifted vertically so as to produce

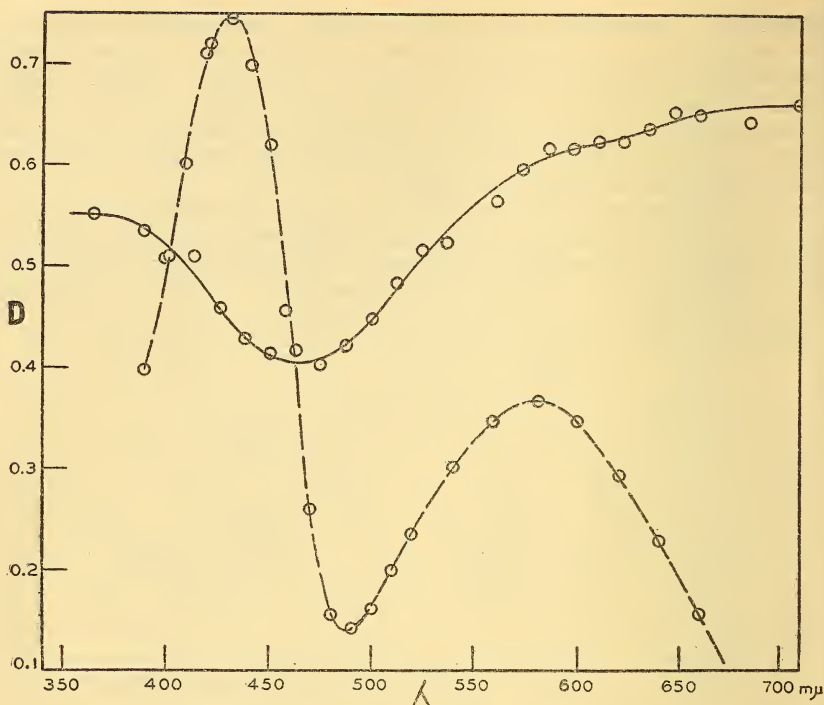


FIGURE 2.—Reversal on plate bathed with pinakryptol green and bromide  
Solid line, density of plate. Dashed line, absorbance of pinakryptol green solution, 1 cm thickness, 0.02 g per liter

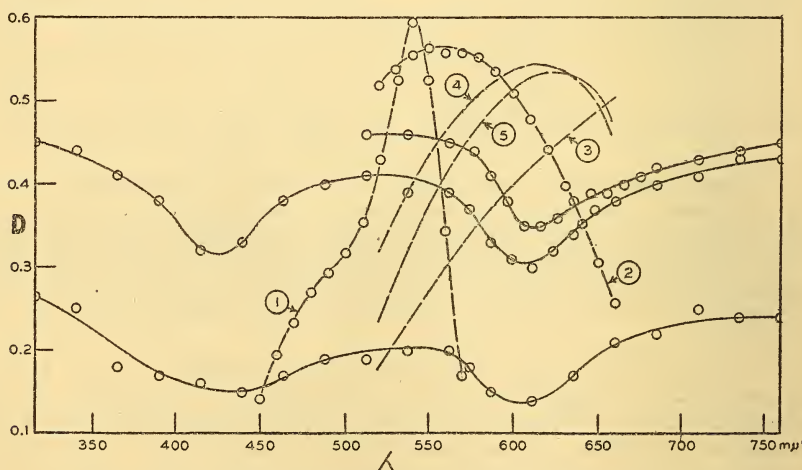


FIGURE 3.—Reversal on plates bathed with fuchsin and bromide

Solid lines represent densities of plates; upper curve made with red filter over slit of spectrograph. Dashed curves: (1) Absorbance of fuchsin solution, 0.0024 g per liter, in 1 cm thickness; (2) minus log reflectance of silver bromide dyed with fuchsin; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution of energy absorbed from a source such as (3) by silver bromide dyed with fuchsin; and (5) log quanta absorbed under these conditions



the minimum confusion in the figures. As a first approximation, the extent of a given photochemical reaction produced by different frequencies not too widely separated may be expected to be proportional to the number of quanta absorbed at each frequency. There are in many cases very large deviations from this theoretical prediction, the higher frequencies (shorter wave lengths) tending to be the more effective, but in the absence of more definite knowledge the effect of varying frequency on a reaction should be compared with the number of quanta absorbed by the material which is believed to be chemically activated by the radiation.

Considering the region covered by curve 5 in Figures 1, 3, and 4, it is obvious that there is excellent correspondence between the reversal

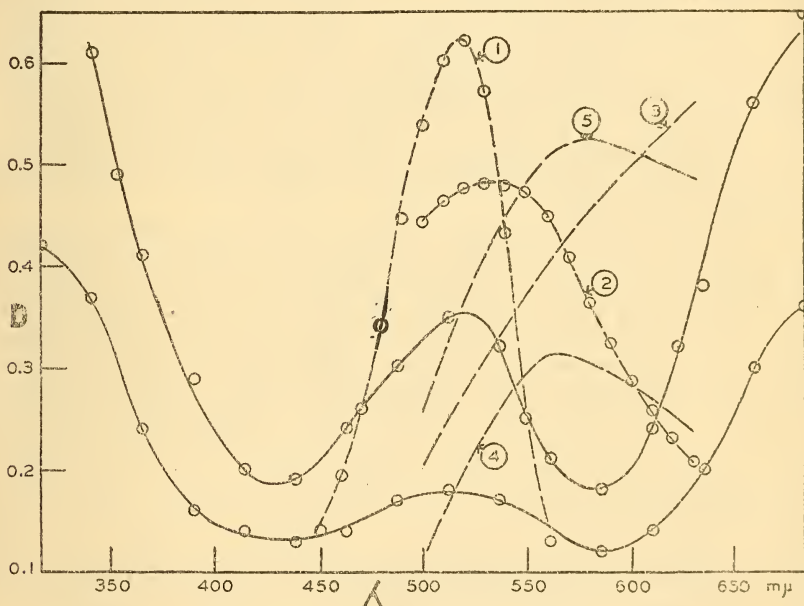


FIGURE 4.—Reversal on plates bathed with safranine and bromide

Solid lines represent densities of plates. Dashed curves: (1) Absorbancy of safranine solution, 1 c.m. thickness, 0.008 g per liter; (2) minus log reflectance of silver bromide dyed with safranine; (3) log relative spectral energy distribution of a black body at 3,000° K.; (4) log spectral distribution of energy absorbed from a source such as (3) by silver bromide dyed with safranine; and (5) log quanta absorbed under these conditions

and the energy quanta absorbed by the dye on the silver bromide. The maxima fall together within the limits of error of the determinations. Figure 2 shows that the relation between reversal and the absorbancy of dye solution is the same for pinakryptol green as for the other dyes. The inevitable conclusion from these data is that the spectral sensitivity of the reversal process depends on the absorption by the dye as directly as does spectral sensitization of the ordinary type. This confirms the earlier work by one of us.<sup>11</sup> It is in direct contradiction to Lüppo-Cramer's conclusion, which we shall be able to show is the result of the misleading impression of spectral sensitivity which may be given by inspection of exposures through filters.

In Figures 3 and 4, there are marked minima of density around 420 to 430 mμ, which are obviously the result of light absorbed by the

<sup>11</sup> Footnote 5, p. 450.

silver bromide itself. The combination of absorption which increases with decreasing wave length and energy incident on the plate in amounts increasing with increasing wave length determines the location of maximum absorption and hence of maximum reversal. In Figures 1 and 2, this maximum of reversal is shifted to 450 and 465  $m\mu$ , respectively, by the absorption of the dye superposed on that of the silver bromide.

In Figure 1, the curve marked *HE* represents the density of a plate coated with pure bromide emulsion which, after the first uniform exposure, had been bathed in 1 per cent potassium bromide solution without dye, then dried and exposed in the spectrograph using a red filter over the slit to eliminate the second order spectrum and stray light of short wave lengths. An exposure of 2½ hours was necessary to produce this limited reversal, which is the true Herschel effect, while the other curves were obtained in 4½ or 13½ minutes using dyes. The maximum reversal lies at about 660  $m\mu$ , and the short wavelength limit is not set by the filter, which cuts off at about 590  $m\mu$ . Hilsch and Pohl<sup>12</sup> found that the maximum of absorption by photo-silver was just short of 700  $m\mu$ . A similar Herschel effect was obtained with the 4-97 pure bromide emulsion used for the reversal experiments with dyes.

Ten-minute exposures were made on all the dyed plates with the same red (Wratten "A") filter. The upper solid line in Figure 3 represents the reversal on a fuchsin-dyed plate under these conditions; the corresponding result on the safranin-dyed plate is omitted because it so nearly coincides with the shorter exposure without filter. There was no measurable reversal on the plates dyed with pinakryptol green and pinakryptol yellow, confirming the results obtained without the filter. It is evident from this that high relative sensitivity to red light is not a common property of all emulsions treated with desensitizing dyes, but occurs only when the dye has the proper absorption. There is no indication from our results that the Herschel effect was increased by the presence of the dyes. There is some sensitivity to red light in every case, as Lüppo-Cramer has demonstrated, but the spectral sensitivity indicates that this should not be called the Herschel effect. Its origin is evident from the data in Figure 5 on long spectrograph exposures. Process plates were given the usual uniform exposure to white light, then bathed with pinakryptol green, pinakryptol yellow and 2-*m*-nitro-styrrylquinoline dimethylsulphate, each at a dilution of 1:5,000 in bromide solution, dried, and exposed in the spectrograph for five minutes without filter, and one hour with the minus blue filter (absorbing radiation of wave length less than 500  $m\mu$ ) over the slit. Curves 1 and 2 show clearly that as the exposure was increased, the region of reversal on the pinakryptol yellow bathed plate extended into the red without indication of a second maximum. The behavior of the plate bathed with pinakryptol green (curve 3) was similar, but there are indications of a secondary maximum about 640  $m\mu$  corresponding to the secondary maximum of absorption of the dye.

The reversal obtained with 2-*m*-nitrostyrrylquinoline dimethylsulphate, one of the simplest dyes of the pinakryptol series, is of particular interest because Lüppo-Cramer<sup>13</sup> has used this as evidence that the reversal effect is independent of the spectral absorption of

<sup>12</sup> Hilsch and Pohl, Proc. 8th. Int. Cong. Phot., p. 29, 1931.

<sup>13</sup> Lüppo-Cramer, reference 3 "Sensibilisierung und Desensibilisierung," pp. 284-285, and Figure 53.

the dye. The 5-minute exposure without filter on the plate treated with this dye produced a reversal which would be represented by a curve quite close to (1) in Figure 5. Examination of curve 4 shows that the slope on the long wave length side is steeper than that of curve 2, made with pinakryptol yellow. This is to be expected, since absorption by 2-*m*-nitrostyrylquinoline dimethylsulphate was found to be very slight at wave lengths over 400  $m\mu$ ; the spectral sensitivity was therefore determined almost entirely by the absorption of the silver bromide.

On visual inspection of the plates made with this material the reversal could be detected to over 700  $m\mu$ , but could not be measured

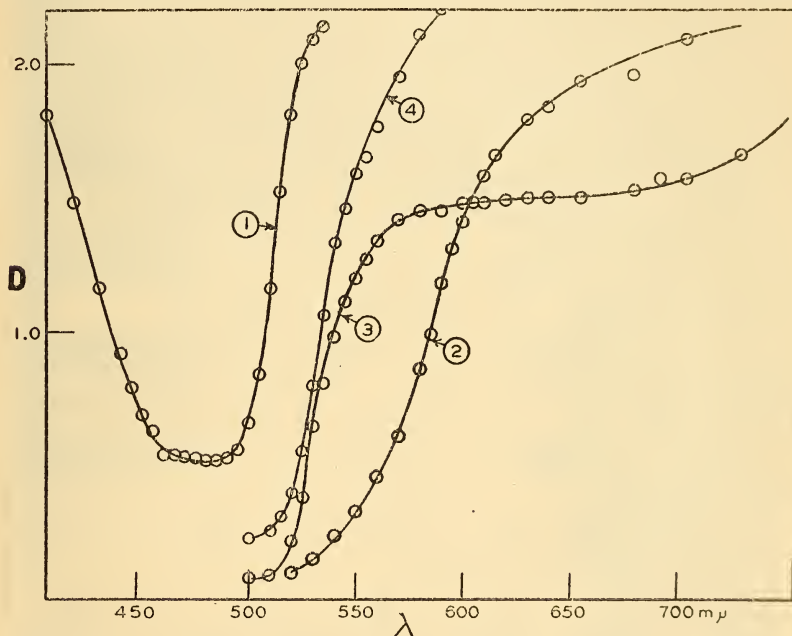


FIGURE 5.—Reversal on plates given long spectrograph exposures

Curve 1, 5-minute exposure; curves 2, 3, and 4, 60-minute exposures with minus blue filter in front of slit of spectrograph. Curves 1 and 2, plate bathed with pinakryptol yellow and bromide; curve 3, plate bathed with pinakryptol green and bromide; and curve 4, plate bathed with 2-*m*-nitrostyrylquinoline dimethylsulphate and bromide.

with any accuracy on the microphotometer because it involved small changes in relatively high densities. Another piece of the same plate used for curve 4 (fig. 5) was exposed behind an Eder-Hecht wedge for two and one-half minutes at 30 cm from a 75-watt, gas-filled lamp. The result is reproduced in Figure 6; the similarity to Lüpbo-Cramer's results (reproduced in his fig. 53) is obvious. The wedge and filter exposure appears to indicate a relative sensitivity to the longer wave lengths which is not confirmed by the quantitative measurements on the spectrograph exposures. The answer appears to lie in what Lüpbo-Cramer has called the "time effect," the marked failure of the reciprocity law for this process in the sense that the photographic effect falls off much less rapidly than the intensity. This shows in the original of the Eder-Hecht exposure as an extraordinarily long



and flat "toe" of the characteristic curve. The consequence is that intensity differences, as judged from the threshold of photographic effect, tend to be equalized and the filter strips on the Eder-Hecht wedge are printed for a distance out of proportion to the relative spectral sensitivity.

## II. EFFECT OF BROMIDE AND DYE CONCENTRATIONS

The curves of Figure 7 represent the results of an experiment which we believe to have considerable theoretical significance. Process

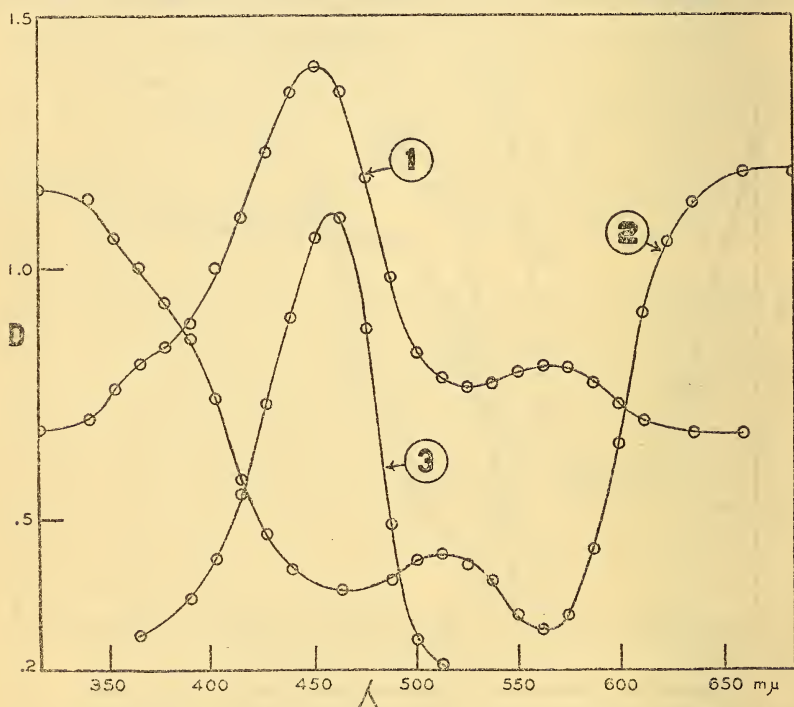


FIGURE 7.—Densities of plates after spectrograph exposures

(1) Preexposed, washed, bathed with solution of safranin in pure water, and dried before spectrograph exposure; (2) preexposed, bathed with solution of safranin and potassium bromide, and dried before spectrograph exposure; and (3) plate of same emulsion, untreated

plates were given suitable preexposures. They were then cut in halves. One half of each was washed for five minutes in running water to remove all soluble bromide, then bathed in a 1: 30,000 solution of safranin in distilled water, dried, and exposed in the spectrograph. The other half was bathed in a 1: 30,000 solution of safranin in 1 per cent KBr solution, then dried and exposed in the spectrograph. All plates were given a series of spectrograph exposures. Curve 1 in Figure 7 represents a plate given 4-second pre-exposure, washed and bathed in safranin without bromide, and exposed 30 seconds in the spectrograph. Curve 2 is for a plate given 8-second preexposure, bathed in safranin plus bromide, and exposed 90 seconds in the spectrograph. Spectral sensitivity was not dependent on the exposure times; densities for the above values were

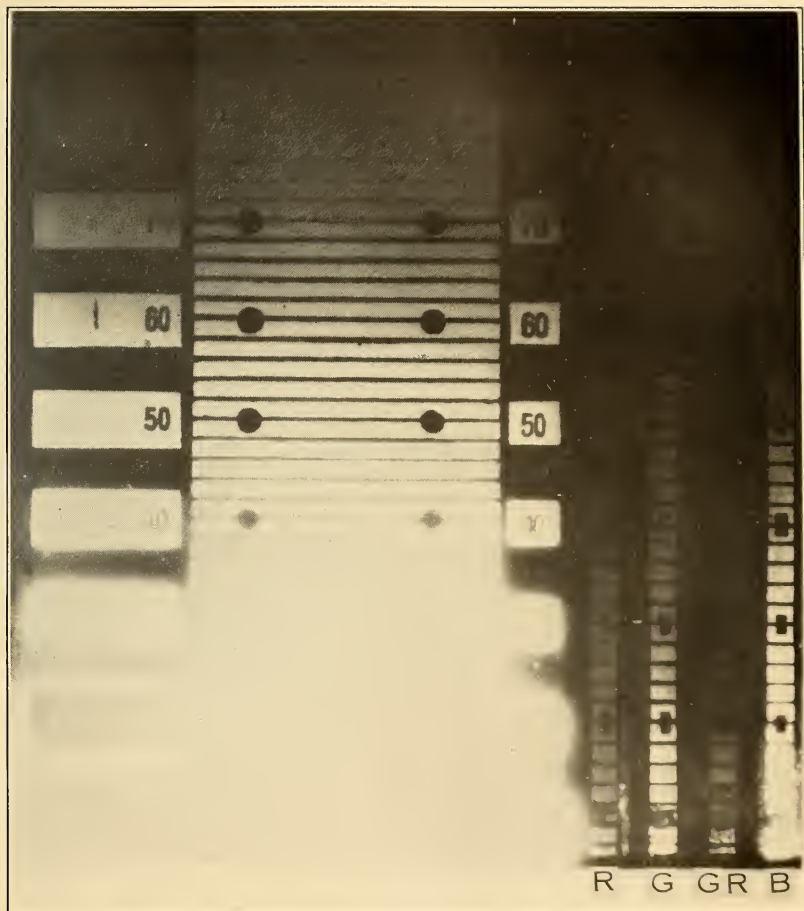


FIGURE 6.—Process plate given uniform exposure to white light, then bathed in a mixed solution of 2-m-nitrostyrylquinoline dimethylsulphate and potassium bromide, dried, and exposed again to incandescent light through an Eder-Hecht wedge

Letters on the narrow strips to the right have the following significance: *R*, red filter; *G*, yellow; *GR*, green; *B*, blue.





chosen as the most suitable for plotting together. Curve 3 in Figure 7 is for an untreated plate of the same kind exposed in the spectrograph for 1 second, without preexposure.

Curve 1 has a maximum of density at  $565\text{ m}\mu$ ; curve 2 has a minimum of density at the same wave length. The maximum at  $565\text{ m}\mu$  in curve 1 obviously indicates sensitization in the ordinary sense by safranin (in spite of its marked desensitizing properties, this dye is described in the 1903 edition of Eder as "a moderately good green sensitizer"). The corresponding minimum in curve 2 demonstrates beyond question that the reversal process is also brought about by light absorbed by the dye. The energy acquired in this way may either form or destroy latent image, depending on the conditions in the emulsion, the silver (or bromide) ion concentration being the variable involved in this experiment.

The maxima in curves 1 and 3, and minimum in curve 2 at  $450$  to  $460\text{ m}\mu$ <sup>13</sup> demonstrate that the same relation holds for radiation absorbed by the silver halide itself as for that absorbed by the dye. Under normal conditions, it is used to form latent image, but in the presence of both dye and soluble bromide it instead destroys image already existing. A maximum of reversal in this region can be detected in Figure 2 of Mauz's paper illustrating exposures on fuchsin bathed plates.

The dye reversal process has generally been associated in the literature, with the longer wave lengths, but there are other illustrations of reversal by radiation absorbed by the silver halide. This is the case for solarization<sup>14</sup> and for reversal on plates which have been converted to iodide.<sup>15</sup>

Further evidence on the nature of the reversal process was obtained from a different type of experiment. Lüppo-Cramer<sup>16</sup> has given characteristic curves of dye reversal with varying concentrations of dye. These curves were made with an intensity scale, and in view of the marked anomalies of the process with regard to intensity it seemed worth while to repeat them with the time scale, which might be simpler to interpret. The experiments were made with safranin on process plates. After constant preexposure, the plates were bathed in solutions of the dye at a dilution of one part of dye to 15, 30, 60, 120, 240, and  $480 \times 10^3$  parts of 1 per cent KBr solution. These dilutions are indicated by the corresponding numbers on the curves of Figure 8. All plates were dried together, then given a nonintermittent sector wheel exposure (0.11 to 30 seconds) to the light from a 500 c. p. "Point-o-lite" lamp at 0.9 m, with a Wratten Minus Blue filter. A second set of plates was exposed 2 to 512 seconds. The combined curves from three test strips for each of the two exposures are plotted in Figure 8 as changes in density from the unexposed portion of the plate. The reproducibility of these curves was relatively poor, although the individual curves for each set of conditions were smooth; the probable error in location of each curve is of the order of 0.2 in density.

The curves for dilutions of  $30$  to  $480 \times 10^3$  fall into a regular progression, the reversal beginning after longer and longer exposure as the

<sup>13</sup> On the pure bromide emulsion used for the exposures recorded in Figure 4, the corresponding minimum lay at  $420$  to  $430\text{ m}\mu$ . The shift is explained by the presence of 3 per cent silver iodide in the silver halide of the process emulsion used for Figure 7.

<sup>14</sup> Reference 5, p. 450.

<sup>15</sup> Renwick, J. Soc. Chem. Ind., vol. 39, p. 156 T, 1920.

<sup>16</sup> Lüppo-Cramer Phot. Ind., vol. 25, p. 1099, 1927. Zeit. f. wiss. Phot., vol. 26, p. 345, 1929.

dilution increases. The most unexpected feature of the data is the formation of a negative image in the early stages of exposure at the highest dilutions, preceding the reversal. This has been observed by Lüppo-Cramer<sup>17</sup> in a few cases of exposures with the intensity scale. With the intensity scale, the reversal may be followed by a negative image (at the highest intensities). This has frequently been observed by Lüppo-Cramer, and confirmed in this laboratory;

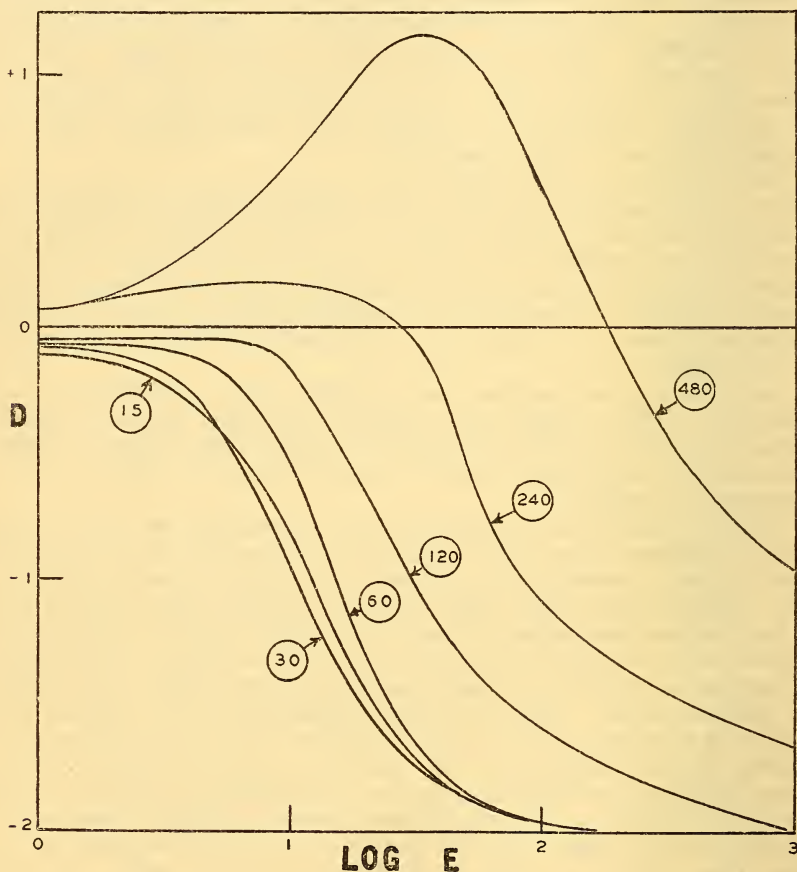


FIGURE 8.—Characteristic curves of reversal process with safranine-dyed plates, made by time-scale exposures

Densities on curves are changes from value produced from original uniform exposure. Numbers on curves multiplied by  $10^3$  indicate dilution of safranine.

it is faintly visible in Figure 6. No indications of this second negative were found in these time-scale exposures; it is possible that it might have occurred if the exposure could have been sufficiently prolonged, but at the lower dilutions of dye the minimum density was maintained without change over a range of exposure of more than 10 times.

The dye at a dilution of  $15 \times 10^3$  produced slightly less effect than at the next higher dilution. Lüppo-Cramer<sup>18</sup> has frequently observed

<sup>17</sup> Lüppo-Cramer, Zeit. f. wiss. Phot., vol. 26, p. 350, 1929. Camera, vol. 6, p. 182, 1928.

<sup>18</sup> See footnote 16, p. 459.

that the more concentrated solutions may produce less effect, and has explained this on the basis of the mutual replacement of adsorbed dye and bromide ions on the silver halide with varying concentrations. It is not excluded, however, that in the plates bathed with the stronger solutions the excess unadsorbed dye may act as a filter to reduce the light absorbed by the dyed silver halide.

### III. DISCUSSION

The outstanding feature of these data is the excellent correspondence between the energy absorbed by the dyed silver bromide and the reversal.

It must be remembered that any photochemical process is necessarily the result of absorption of radiant energy by the reacting system. In the plates as exposed in the spectrograph there are three materials possessing selective absorption in the visible spectrum and near infra-red. These are the silver halide, the dye, and the products of the first exposure (probably, but not positively identical with the latent image). Absorption by silver sulphide (sensitivity nuclei) may also reasonably be included with the products of exposure. Silver halides have strong selective absorption for radiation of wave lengths less than  $500\text{ m}\mu$ ; the dyes have strong selective absorption for regions depending on the dye; and the products of exposure, plus silver sulphide, have selective absorption for the red and near infra-red,<sup>19</sup> which is extremely weak because of the minute traces present. Energy absorbed by any of these three from radiation in or near the visible region is a potential source of photochemical reaction in the plate, since the absorbing molecules must thereby become "excited" or "activated." The energy of activation may simply be transformed to heat, without reaction; an unknown proportion is so lost in the plates under discussion. A chemical reaction may follow activation either because the activated molecule itself breaks down, or because the energy of activation is transferred<sup>20</sup> to some other species of molecule, causing it to be chemically activated and therefore to react. This second process is commonly termed sensitization or photochemical catalysis. The spectral sensitivity of the plate will be determined by the primary process, the absorption of energy; but the photochemical yield from a given energy absorption (expressed when possible in terms of molecules reacting per quantum of energy absorbed) depends enormously on secondary chemical processes following the primary absorption; that is, on the chemistry of the system in which the absorption takes place.

Assuming anything like equal yield in terms of molecules reacting per quantum of light absorbed in different parts of the spectrum, we would therefore expect a marked reaction to be produced by the spectral regions absorbed by the silver bromide and the dye, respectively, and a very slight one in the red where the selective absorption by the latent image is strongest. The observed photographic reversal corresponds to this assumption. The plates bathed with fuchsin and safranin, on which the two main regions of absorption are far enough

<sup>19</sup> See footnote 12, p. 456.

<sup>20</sup> This process in gases occurs largely by "collision of the second kind." This same term has been applied by Leszyuski and others to hypothetical energy transfer from sensitizing dyes to silver halide; without denying the possibility of such energy transfer in photographic sensitization, it seems quite undesirable in the present state of our knowledge to apply the term of "collision" to a process occurring in the solid state.



separated so that they can be clearly distinguished, were most sensitive in the region around 420 to 430  $m\mu$ , since the reversal was as strong as in the longer wave lengths, while the energy received on unit area was much less. As the absorption could not be measured quantitatively in the plates, it is impossible to estimate the relative quantum yield in the two regions.

In the opinion of the writers, the results given by Mauz<sup>21</sup> are in agreement with ours, in spite of their superficial differences. His use of a prism spectrograph with an incandescent source of about 2,850° color temperature caused a great concentration of energy in the red end of the spectrum. A simple calculation from the scale of his published figures and the energy distribution of such a source shows that the plates received about 85 times as much energy per unit area in the spectral region 600 to 700  $m\mu$  as in the region 400 to 420  $m\mu$ , as against a ratio of 6 for the same regions in our instrument. His exposures were, furthermore, so long as to produce reversal over the entire visible spectrum in every case, thus tending to obscure the differences between the plates bathed in different dyes. However, the influence of the absorption by the dye is clearly evident from his figures. The plates bathed with fuchsin and phenosafranine have marked maxima in the red which are not shared by the other dyes. That bathed with pinakryptol yellow has its strongest reversal between 400 and 500  $m\mu$ . The results with pinakryptol green are more difficult to interpret, but the appearance of the plates between 400 and 500  $m\mu$ , where the central part of the spectrum is dark and the edges light, is most probably explained by a maximum sensitivity in this region, combined with overexposure sufficient to produce the second negative. The light edges are the result of reversal in the region of irradiation from the more strongly exposed central portions. A similar effect may be detected in spectrum 8 (fig. 2) of the paper by Carroll. In Figure 2 of Mauz's paper the reversal in the region of absorption by the silver halide, where it is distinct from that of the dye, was obscured by the low intensity incident on this portion of the plates, but a secondary maximum is detectable at about 460  $m\mu$ .

Conclusions based on a process as complicated as this must be accepted with considerable caution, but the field for speculation is extensive and tempting. The theory of the true Herschel effect (reversal without dyes) is apparently simple. Absorption of red and infra-red radiation by the products of the first exposure causes them to react, naturally destroying their effectiveness as latent image whether the reaction is regression to the original form or not. The photographic sensitivity is very low, corresponding to very weak absorption; emulsions containing iodide show the Herschel effect with great difficulty because the traces of absorption by brom-iodide in the longer wave lengths cause a reaction (latent image formation) which counteracts the Herschel effect at least photographically, and probably chemically. The Herschel effect may be materially increased by changes in the chemistry of the emulsion, increase in bromide ion concentration and the presence of traces of copper salts being definitely established as promoters of the effect. As alkali bromides have no absorption in the visible region their effect must be on the secondary chemical processes following absorption.

<sup>21</sup> See footnote 4, p. 450.

The possible views of the effect of the dyes on reversal are that: (1) Energy absorbed by the dye is used in the reversal reaction, either directly or indirectly, and (2) the dye, like soluble bromide, increases the effect of absorption of energy by other materials, via the secondary chemical processes; this is the view taken by Lüppo-Cramer.<sup>22</sup> These theories are not mutually exclusive, since the second may apply independent of the first. The tendency to reversal in the presence of the dye certainly exists, since the rate of fading of the latent image in the dark is quite appreciable, especially when soluble bromide as well as desensitizer is present. This is essentially the same reaction, going on slowly under thermal activation of the dye molecules, and rapidly under photochemical activation. Further evidence that the dye causes a tendency to regression independent of its absorption of light comes from the observed reversal by radiation which must be absorbed by the silver bromide itself. In this case, we must assume that the energy absorbed by the silver bromide is transferred to the latent image. This is reasonable, since the converse process—spectral sensitization of silver bromide by colloidal silver—is a well-known phenomenon. Energy absorbed by the products of exposure must be effective in producing reversal in the presence of the dye, but it is nearly negligible in comparison to that acquired by the other absorbents. Our data fail to show that the sensitivity of the dyed plates to the red and infra-red resembles what might be expected if the true Herschel effect played any appreciable part in the reversal process. We accordingly consider that it is unjustifiable to identify the Herschel effect and the dye reversal to the extent which has been common in the literature.

The analogy between sensitization in the ordinary sense and the reversal phenomena under discussion is evident from the data on spectral sensitivity. It receives considerable confirmation from the effect of variables common to the two processes. The most important of these is the silver (or bromide) ion concentration. Increase in silver ion concentration (up to the point where fog interferes) greatly improves<sup>23</sup> the effectiveness of ordinary sensitization; conversely, increase in bromide ion concentration by addition of soluble bromide increases reversals by desensitizing dyes,<sup>24</sup> and decreases sensitization. We have shown in Figure 7 that the action of safranin, as the result of activation by light which it selectively absorbs, may be either, an increase or a decrease in density, depending on the bromide ion concentration of the emulsion. We have already expressed the opinion that the bromide ion concentration alters the oxidation-reduction potential of the silver halide grain with respect to its environment through the varying adsorption of bromide or silver ions to its surface. Further evidence that the reversal is an oxidation process is given by Lüppo-Cramer's observations<sup>25</sup> that photo-silver may be bleached by pinakryptol yellow plus bromide in light, and that under some conditions desensitization and reversal may be appreciably decreased by the presence of reducing agents, such as nitrite. We also have the increase in sensitization (hypersensitization) by reducing

<sup>22</sup> "Die an und für sich, besonders in langwelligen Gebiete vorhandene Tendenz zur Umkehrung der Bromsilberzersetzung (Herscheleffekt) durch die Farbstoffe infolge Keimisolierung unterstützt wird." (Handbuch, vol. 3, pt. 3, p. 285.)

<sup>23</sup> Carroll and Hubbard, B. S. Jour. Research, vol. 9 (RP488), p. 529, 1932.

<sup>24</sup> Lüppo-Cramer, Die Kinteknik, vol. 11, p. 399, 1929.

<sup>25</sup> Lüppo-Cramer, Phot. Ind., vol. 28, p. 365, 1930.

agents,<sup>26</sup> and the increase in reversal by oxidizing agents.<sup>27</sup> These effects are somewhat erratic and difficult to reproduce, but appear to be real. The evidence establishes a strong presumption that sensitization and reversal by dyes are not only photographically but chemically opposite directions of the same process.

The nature of the characteristic curves with varying dye concentrations, in Figure 8, may be interpreted by the hypothesis that reversal begins when a given oxidation potential is reached. Oxidation potential under constant illumination should tend to increase with increasing concentration of dye, and with increase in latent image. The required potential may then be built up either by more concentrated dye and less image, or by an increase in image with the most dilute dyes. Once the reversal process is started, it may be able to continue without a decrease in reduction potential to the original value, if the quantity of dye is assumed to be chemically equivalent to many times the silver of the latent image.

Sensitization and reversal by dyes may be both brought about by energy absorbed by the dye. The simplest and most probable theory is that the dye, chemically activated by absorption, then takes part in an oxidation or reduction reaction with silver bromide or photo-silver. The evidence from spectral sensitivity, however, does not distinguish between this case and the transfer of the activation energy from the dye to another material which then reacts.

WASHINGTON, February 13, 1933.

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<sup>26</sup> Bokinik, *Zeit. f. wiss. Phot.*, vol. 30, p. 330, 1932; Carroll and Hubbard, *B. S. Jour. Research*, vol. 10 (RP525), p. 211, 1933.

<sup>27</sup> Lüppo-Cramer, *Die Kinotechnik*, vol. 10, p. 506, 1928.





